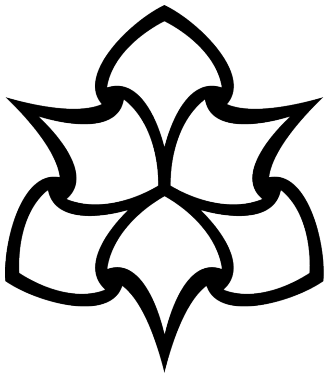

Role of Phenol and Phosphite Antioxidant Combinations in the Thermal Stabilisation of Metallocene LLDPE (mLLDPE): Optimisation and Performance and Influence of Metal Stearates on Multiple Extrusions

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1. ABSTRACT

This study progresses our earlier studies and takes the performance characteristics of a 1:1 Irganox 1010: Irgafos 168 combination at 1000ppm each through multiple extrusion processes in a metallocene LLDPE (mLLDPE) investigating for the first time the role of a broad range of calcium and zinc stearates based on animal vs vegetable origins of the stearine function. In this case performance was assessed using Melt Flow Rate (MFR) coupled with HPLC to determine not only the additive depletions after processing but also the rate of production of the phosphite to phosphonate. Comparative control studies were also undertaken on the single use of the separate antioxidants. Both stearates influenced the activity of the antioxidants in particular their consumption. A greater consumption after the third and fifth extrusion was observed with metal stearates produced from the vegetable stearine. Moreover, zinc stearates seemed to provide a greater detrimental effect than calcium stearates. Hydroperoxide analysis on the stearates confirmed the animal stearine to contain higher levels of peroxides which may contribute toward the higher activity. The optimisation of the thermal stabilisation of the metallocene polyethylene (mLLDPE) has also been investigated in this study. Several conditions of stability were determined for the determination of the optimal antioxidant (phenol:phosphite) ratio. The main parameter was high melt stability for a maximum processing stability of the final package via DSC analysis (OIT) coupled with assessments of embrittlement time (oven ageing) and yellowness index. Long-term stability against thermo-oxidation was considered coupled with a consideration of their hydrolytic stability as a complicating factor. In this work the (phenol/phosphite) antioxidant formulations with two different phenolic antioxidants (Irganox 1010, Irganox 1076) and six different phosphite antioxidants (Irgafos 168, Irgafos P-EPQ, Adekastab PEP-8, Adekastab PEP-36, Adekastab PEP-24G, Adekastab HP-10) were assessed at different levels taking into account the various criteria for optimal performance providing hitherto useful information than many prior studies on 1:1 percentage ratios i.e. how much phosphite is required for optimal activity. A question often posed in the field with the results concluding an interesting unified optimum ratio of 4:1 (for most antioxidants studied) taking into account all the critical parameters.

2. INTRODUCTION

Metallocene polyethylene are notable for their narrow molecular weight distribution (Mw/Mn = 2 to 3) and in particular for the uniformity of the comonomer distribution along the chain length. Indeed, modern metallocene catalysts only have one type of catalytically active site (single-site catalysts); the homogenous metallocenes produce then much more homogeneous polyolefins with narrower MMDs. On the other hand, conventional Ziegler-Natta (ZN) catalysts consist of a variety of centers with differing catalytic activity, resulting in complex product mixes; Polymers produced in this way are characterised by their broad molar mass distributions (MMD), whereas copolymers additionally have high chemical in-homogeneities, i.e. the comonomer is predominantly incorporated in the wax-like, low-molar mass fractions. With metallocene copolymers, the comonomers are distributed evenly over the chain lengths. This means that metallocene polyolefins and metallocene olefin copolymers have significantly lower contents of low-molar mass, wax-like fractions. This guarantees excellent organoleptic properties. These molecular characteristics leads also to superior mechanical and optical properties. However, the narrow molecular weight distribution also has certain implications for processing.

Metal stearates are commonly used as acid scavengers in combination with sterically hindered phenolic antioxidants and phosphite processing stabilisers for the stabilisation of polyolefins. Indeed, the use of such antacid co-additives is essential in the stabilisation of Ziegler-Natta polyolefins; such polymers contain acidic catalyst residues such as chlorine from $TiCl_3$, AlR_2Cl or $MgCl_2$ that can cause corrosion of the processing equipment and catalyse peroxide decomposition, hence affecting polymer oxidative stability. Such acidic residues are also known to promote dealkylation of phenolic antioxidants, and therefore enhance the discoloration in the polymer [1]. Early studies [1] showed that metallic stearates could prevent colour formation in Ziegler-Natta polyolefins stabilised with hindered phenolic antioxidants. Indeed, it has been demonstrated that titanium catalyst residues (>Ti-Cl) could interact with sterically hindered phenolic antioxidants and result in the formation of coloured species [2].

In the case of chromium-based polyethylenes, the benefits of antacid agents are more variable since remnant chromium oxide catalyst residues are neutral and do not require the addition of acid neutraliser. However, the presence of acid scavenger such as zinc stearate did improve colour performance in Phillips-type HDPE, while slight antagonism was observed with calcium stearate [1]. The development of the latest metallocene catalyst technology has introduced polyolefins with unique properties and low catalyst residues content. However, the use of zirconocene chloride catalyst may require the need of acid scavengers like in Ziegler-type polymers.

It is well recognised that the presence of such acid neutralisers can significantly affect the overall performance of the whole additive package for polyolefin stabilisation [3]. The effect of metal stearate antacids may depend strongly on the polymer used as well as the co-additives present in the stabiliser package. However, the inherent properties of those salts of fatty acids may have to be also taken into consideration. Indeed, metallic stearates are available in a broad range of grades, and the origin of the stearine sources used for the formation of such acid scavengers has never been considered in the literature as a factor influencing the response of such additive in terms of processing colour and stability in polyolefin stabilisation.

Recent studies on the influence of zinc stearate in the long-term thermal stabilisation of a chromium-based HDPE with phenol/phosphite stabiliser blends also showed antagonistic effect of such antacid [4]. Interesting results were observed in terms of interactions between phenolic antioxidant (Irganox 1010) and zinc or calcium stearate. Indeed, second derivative UV evaluation of stabilised HDPE films showed that a higher decomposition rate of the phenolic antioxidant during oven ageing at 110°C was observed in the presence of both acid scavengers. Furthermore, a single pass extrusion experiment also emphasised the antagonistic effect of zinc stearate when added to the phenolic antioxidant alone or with the phenol/phosphite blend. Antagonistic effects have also been recorded in HDPE for antioxidant blends in the presence of calcium stearate [5]. In some formulations complexation and exchange by the phosphite with the stearate ligand was identified. These interesting observations led to the investigation of the consumption of both antioxidants, i.e. Irganox 1010 and Irgafos 168, during the multiple extrusion experiments proposed here.

The purpose of this study was to examine the influence of metal stearates further (calcium and zinc stearates) on the melt stabilisation performance in combinations with a hindered phenolic antioxidant (Irganox® 1010) and a phosphite processing antioxidant (Irgafos® 168) in a standard metallocene LLDPE using melt flow rate (MFR) and HPLC. This work investigates particularly the influence of both the origin of the stearine blend (i.e., animal or vegetable) used for the production of the metal stearates and the type of metallic stearate, i.e., zinc and calcium stearate. Peroxide levels in the stearates have also been assessed. The phenolic antioxidant, the phosphite antioxidant and the metal stearate were all used at a concentration of 1000 ppm each for suitable analysis by HPLC for detection purposes. Lower concentration values at long processing times (x5) would inevitably result in zero levels of detection. A control formulation containing only the phenolic and phosphite antioxidants, but no metal stearate, was also used as a reference. This investigation following our previous investigation [6] provides a useful and more detailed analysis of the complexities of stabilising interactions over five extrusions with a wide range of types of metal-based ant-acid stearines of different origins.

Although there have been numerous investigations into the complexities and stabilising performance of additives in polyolefins [4-15] many have dealt with earlier non-metallocene type polymers, light stabilisation or antioxidant combinations usually at single ratios and often at 1:1. Thus, many have provided useful stability data and interactions but in most cases do not provide the complete picture where for example either mole ratios or percentage ratios can exhibit major performance characteristics and in some cases abnormalities. To provide a useful follow-up of the study here we have also investigated a detailed analysis of the stabilisation of mLLDPE of two phenolic antioxidants (namely Irganox 1010 and 1076) coupled with a range of phosphite antioxidants of varying hydrolytic stability at different percentage ratios. In this analysis a whole range of methodologies have been utilised, compared and cross-analysed to determine optimum performance through carbonyl index, DSC (OIT) and Yellowness Index. Overall, all the data provides a very useful technological outcome in verifying the maximum stabilising ratio at 4:1 in order to satisfy most of the criteria used with the phenolic playing the major role and the phosphite acting as an initial protector at a much lower level.

3. EXPERIMENTAL

3.1 Materials

The polymer mLLDPE (Repsol) was analysed for a range of metal catalyst residues (aluminium, titanium, chromium and zirconium) using an inductively-coupled plasma (**ICP)** emission spectrophotometry via VARIAN Vista AX CCD Simultaneous ICP-AES instrument. Only 0.1ppm of Zr was found-no other metals were present.

Antioxidants Chemical Names

The antioxidants and ant-acids were as follows:

Irgafos 168 (Clariant): Tris(2,4-di-tert-butylphenyl) phosphite

Irgafos PEP-Q (Clariant): Tetrakis(2,4-di-tert- butylphenyl) [1,1'-biphenyl]-4,4'-diylbis(phosphonite

Adekastab PEP-8 (Asahi Denka Kogyo K.K.): distearyl pentaerythritol diphosphite

Adekastab PEP-36 (Asahi Denka Logyo K.K.): bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite

Adekastab HP-10 (Asahi Denka Kogyo K.K.): 2,2-methylenebis (4,6-di-tert- butylphenyl)octylphosphite

Adekastab PEP 24-G (Asahi Denka Kogyo K.K.): bis-(2,4-di-tbutylphenyl) pentaerythritol-diphosphite

Irganox 1010 (Clariant): Tetraalkofen BPE; Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)

Irganox 1076 (Clariant): Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate; Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate

Zinc and Calcium Stearates (Unichema International)

3.2 Polymer Film Preparation

All additives were solvent blended using dichloromethane followed by evaporation. Each sample was pressed with a steam press at a temperature of about 160°C. The obtained thickness lied between 150-250 μm. Small pieces of films were then mounted onto aluminium holders for the thermo-oxidative degradation. The thickness has been set at 200 ± 5 μm in order to allow the same rate of degradation for all samples. Formulations prepared are as follows in Table 1-4.

Table 1

0.1% w/w Phenolic Formulations

Sample	Formulation
1	0.1% w/w IRGANOX 1010
32	0.1% w/w IRGANOX 1076

Table 2

0.1% w/w Phosphite formulations

Sample	Formulation
6	0.1% w/w IRGAFOS 168
11	0.1% w/w IRGAFOS P-EPQ
16	0.1% w/w ADEKASTAB PEP-8
21	0.1% w/w ADEKASTAB PEP-36
26	0.1% w/w ADEKASTAB HP-10
31	0.1% w/w ADEKASTAB PEP 24-G

Table 3

0.1% w/w/ Irganox 1010 + Irgafos 168 Combinations

Sample	IRGANOX 1010	Phosphite
2	0.08% w/w	0.02% w/w IRGAFOS 168
3	0.06% w/w	0.04% w/w IRGAFOS 168
4	0.04% w/w	0.06% w/w IRGAFOS 168
5	0.02% w/w	0.08% w/w IRGAFOS 168
7	0.08% w/w	0.02% w/w IRGAFOS P-EPQ
8	0.06% w/w	0.04% w/w IRGAFOS P-EPQ
9	0.04% w/w	0.06% w/w IRGAFOS P-EPQ
10	0.02% w/w	0.08% w/w IRGAFOS P-EPQ
12	0.08% w/w	0.02% w/w ADEKASTAB PEP-8
13	0.06% w/w	0.04% w/w ADEKASTAB PEP-8
14	0.04% w/w	0.06% w/w ADEKASTAB PEP-8
15	0.02% w/w	0.08% w/w ADEKASTAB PEP-8
17	0.08% w/w	0.02% w/w ADEKASTAB PEP-36
18	0.06% w/w	0.04% w/w ADEKASTAB PEP-36
19	0.04% w/w	0.06% w/w ADEKASTAB PEP-36
20	0.02% w/w	0.08% w/w ADEKASTAB PEP-36
22	0.08% w/w	0.02% w/w ADEKASTAB HP-10
23	0.06% w/w	0.04% w/w ADEKASTAB HP-10

24	0.04% w/w	0.06% w/w ADEKASTAB HP-10
25	0.02% w/w	0.08% w/w ADEKASTAB HP-10
27	0.08% w/w	0.02% w/w ADEKASTAB PEP 24-G
28	0.06% w/w	0.04% w/w ADEKASTAB PEP 24-G
29	0.04% w/w	0.06% w/w ADEKASTAB PEP 24-G
30	0.02% w/w	0.08% w/w ADEKASTAB PEP 24-G

Table 4

0.1% w/w/ Irganox 1076 + Irgafos 168 Combinations

Sample	IRGANOX 1076	Phosphite
33	0.08% w/w	0.02% w/w IRGAFOS 168
34	0.06% w/w	0.04% w/w IRGAFOS 168
35	0.04% w/w	0.06% w/w IRGAFOS 168
36	0.02% w/w	0.08% w/w IRGAFOS 168
37	0.08% w/w	0.02% w/w IRGAFOS P-EPQ
38	0.06% w/w	0.04% w/w IRGAFOS P-EPQ
39	0.04% w/w	0.06% w/w IRGAFOS P-EPQ
40	0.02% w/w	0.08% w/w IRGAFOS P-EPQ
41	0.08% w/w	0.02% w/w ADEKASTAB PEP-8
42	0.06% w/w	0.04% w/w ADEKASTAB PEP-8
43	0.04% w/w	0.06% w/w ADEKASTAB PEP-8
44	0.02% w/w	0.08% w/w ADEKASTAB PEP-8
45	0.08% w/w	0.02% w/w ADEKASTAB PEP-36
46	0.06% w/w	0.04% w/w ADEKASTAB PEP-36
47	0.04% w/w	0.06% w/w ADEKASTAB PEP-36
48	0.02% w/w	0.08% w/w ADEKASTAB PEP-36
49	0.08% w/w	0.02% w/w ADEKASTAB HP-10
50	0.06% w/w	0.04% w/w ADEKASTAB HP-10
51	0.04% w/w	0.06% w/w ADEKASTAB HP-10
52	0.02% w/w	0.08% w/w ADEKASTAB HP-10
53	0.08% w/w	0.02% w/w ADEKASTAB PEP 24-G
54	0.06% w/w	0.04% w/w ADEKASTAB PEP 24-G
55	0.04% w/w	0.06% w/w ADEKASTAB PEP 24-G
56	0.02% w/w	0.08% w/w ADEKASTAB PEP 24-G

3.3 **DSC analysis (OIT)**

Thermal stability of the samples was assessed by differential scanning calorimetry (DSC) via the determination of an oxygen induction time (OIT) using the standard onset temperature set at 200C.

3.4 **Carbonyl Index**

Rates of polymer oxidation were measured by monitoring the rate of formation of the non-volatile carbonyl oxidation products in the region 1500-1800 cm^{-1} using a BIORAD FT-IR spectrometer. Carbonyl growth in this region of the spectrum was determined by the carbonyl index defined as follows:

Carbonyl index = A/d x 100 where A = absorbance
d = film thickness (⌈m)

Embrittlement time will then be recorded, assuming that embrittlement time is defined as the oven ageing time associated to a carbonyl index value of 0.1.

3.5 **Colour Measurements**

Yellowness Index measurements were carried out on a GretaMacbeth Spectroeye Colorimeter (Colour data Systems Ltd., Wirral, UK) according to ASTM D1925.

3.6 **Hydrolytic Stability**

The phosphite stabilisers wer exposed in a pyrex dish in a water vapour chamber set in an oven at 80 ^{o}C. using HPLC the additives were analysed until no phosphite could be detected.

3.7 **Melt Flow Index (Rate)**

This parameter was measured using a Ray-Ran® *Melt Flow Indexer* capillary melt viscometer by applying a standard weight and a melt temperature of 190°C, in accordance with ASTM D1238.

The MFI decline was defined as:

$$MFI_{decline} = \frac{MFI}{MFI_{initial}} \times 100$$

3.8 **Hydroperoxides: Iodometric method**

Hydroperoxide measurement was assessed by a standard iodometric method.

In the iodometric method is based on the reduction of the peroxide bond by iodide ion (I^-) to iodine (I_2), and in presence of iodide excess, the concentration of the resulting intensively coloured non-volatile tri-iodide ion I_3^- can be measured spectrophotometrically.

Stearate samples (0.5 g) were refluxed for 30 minutes with 10 ml of a mixture of glacial acetic acid (100%, GPR™ BDH Chemicals Ltd) and propan-2-ol (99.8%, CHROMASOLV® Riedel-deHaën, HPLC grade) at a ration by volume of (5:95/acetic acid:2-propanol) in the presence of 0.1 g of Sodium Iodide (99%, FISONS plc). At the end of the reflux period, the solution was cooled for 5 minutes, and the I_3^- formed during the peroxide decomposition was determined on a Perkin Elmer Lambda 7 UV/Vis spectrophotometer at 420 nm in a 1 cm quartz cell. The calibration curve was obtained using cumene hydroperoxide (80%, BDH Chemicals Ltd) as a standard.

3.9 **Quantification of antioxidants**

Quantification of antioxidant was measured after each extruder pass via HPLC analysis of solvent extracts. Antioxidants were extracted by a standard solvent extraction procedure of polymer films in dichloromethane CH_2Cl_2 (b.p: 40°C) for 4 hours since methylene chloride has been shown to be a good extraction solvent without risking hydrolysis breakdown of the phosphite ester Irgafos® 168.

The HPLC analysis was carried out with a Hewlett Packard *Series 1100* with a diode-array UV detector set at 230 nm. A 20µL sample was injected onto a HyPURITY™ Elite HYPERSIL® (150×4.6mm) ODS 5µ C_{18} reverse phase column used at ambient temperature and eluted with a mobile phase mixture of propan-2-ol (99.8%, CHROMASOLV® Riedel-deHaën, HPLC grade) and acetonitrile (99.9%, E CHROMASOLV® Riedel-deHaën, HPLC & UV grade) at a ratio by volume of (20:80/isopropanol:acetonitrile) at a flow rate of 1.0mL/min. The column back-pressure was 48 ± 2 bar. The data system for collection was HPLC 2D Chemstation Rev. A.05.XX software. The retention times of antioxidants are summarised in 5.

Table 5. Retention times of antioxidants

Antioxidants	Irganox® 1010	Irgafos® 168
R_t (minutes)	2.9	7.1

3.10 **Multiple extrusion experiment**

Multipass extrusion can be regarded as a type of accelerated ageing for simulating processing conditions. The method involves repeatedly passing the polymer through an extruder and then collecting the samples after each pass. The multiple extrusions were carried out on a Betol® BTS 30 laboratory corotating twin-screw compounding extruder (screw length = 690 mm, screw diameter = 30 mm, L:D = 23:1) at a melt temperature of 230°C and a screw rotation speed of 80 rpm. The tubular extrudate was cooled in a Betol® *model 119* water bath and pelletised with a cutting device. All extrusions were done in air. The temperature profile is described in 6.

Table 6. Temperature profile for the multiple extrusion experiment

Extruder temperature (°C)	Melt temperature (°C)
Barrel zones	*Die zone*
210 / 210 / 215 / 220 / 225	230

In the case of virgin polymer powders, four extrusions were successively carried out. In the case of stabilised polymer pellets, three extrusions were successively carried out since the first extrusion pass was considered as the compounding step, which was done on a commercial scale.

4. RESULTS AND DISCUSSION

4.1 Influence of metal stearates during processing

In the case of chromium-based polyethylenes, the benefits of antacid agents are more variable since remnant chromium oxide catalyst residues are neutral and do not require the addition of acid neutraliser. However, the presence of acid scavenger such as zinc stearate did improve colour performance in Phillips-type HDPE, while slight antagonism was observed with calcium stearate [6]. The development of the latest metallocene catalyst technology has introduced polyolefins with unique properties and low catalyst residues content. However, the use of zirconocene chloride catalyst may require the need of acid scavengers like in Ziegler-type polymers.

It is well known that acid neutralisers can significantly affect the overall performance of the whole additive package for polyolefin stabilisation [2,3]. The effect of metal stearate antacids may depend strongly on the polymer used and the co-additives present in the stabiliser package. However, the inherent properties of those salts of fatty acids may have to be also taken into consideration. As stated above the purpose of this study was to examine the influence of metal stearates (calcium and zinc stearates) on the melt stabilisation performance in combinations with a hindered phenolic antioxidant (Irganox® 1010) (I1010) and a phosphite processing antioxidant (Irgafos® 168) (I168) in a standard metallocene LLDPE. This work investigates particularly the influence of both the origin of the stearine blend (i.e., animal or vegetable) used for the production of the metal stearates and the type of metallic stearate, i.e., zinc or calcium stearate. The phenolic antioxidant, the phosphite antioxidant and the metal stearate were all used at a concentration of 1000 ppm. A control formulation containing only the phenolic and phosphite antioxidants, but no metal stearate, was used as a reference. The MFR of formulations containing these additives were measured. The MFR data are presented in Figure 1.

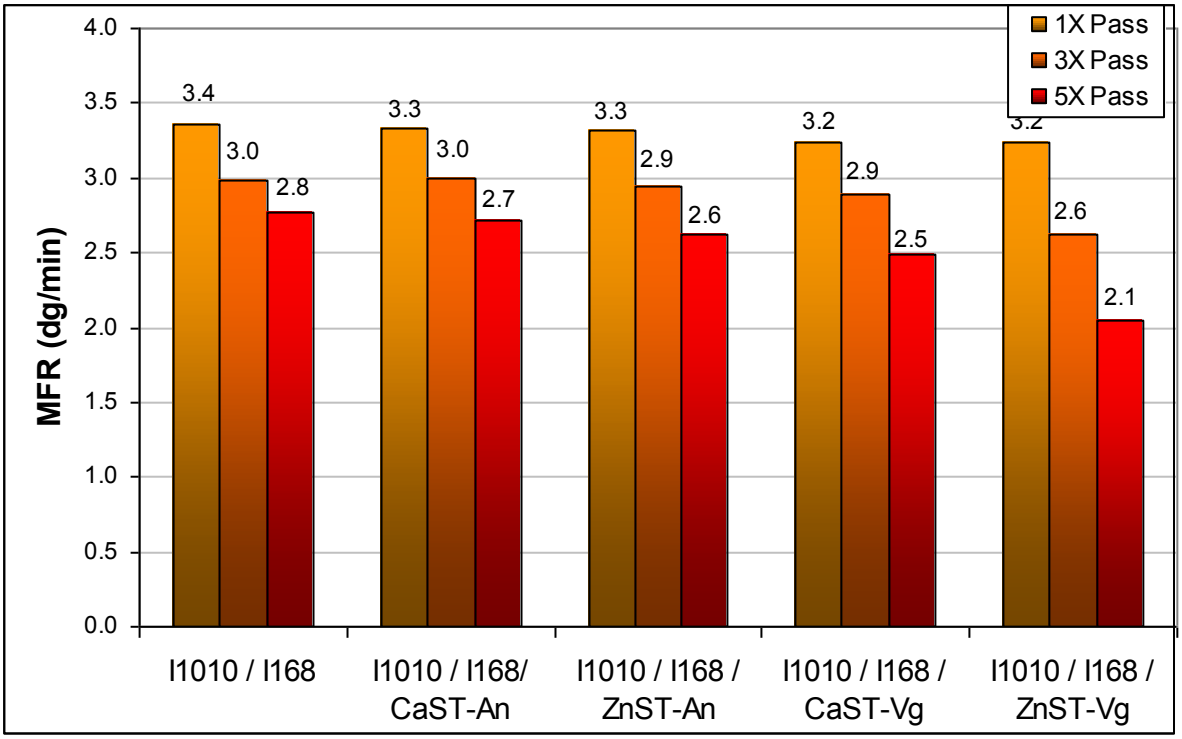

Figure1. MFR (dg/min) of mLLDPE stabilised with a phenolic AO I1010 (1000 ppm), a phosphite AO I168 (1000 ppm), and a metal stearate (1000 ppm) after the first, third and fifth extrusion pass at 200°C

The presence of both grades of metal stearate, i.e., animal or vegetable, promoted a slight antagonistic effect in terms of melt viscosity protection. The vegetable grade displayed a more pronounced antagonism than the animal-based metal stearates. Furthermore, the zinc stearate appeared to exhibit a more detrimental effect than calcium stearate.

Recent studies on the influence of zinc stearate in the long-term thermal stabilisation of a chromium-based HDPE with phenol/phosphite stabiliser blends also showed antagonistic effect of such antacid [4-6,8]. Interesting results were observed in terms of interactions between phenolic antioxidant (I1010) and zinc or calcium stearate. Indeed, second derivative UV evaluation of stabilised HDPE films showed that a higher decomposition rate of the phenolic antioxidant during oven ageing at 110°C was observed in the presence of both acid scavengers. Furthermore, a single pass extrusion experiment also emphasised the antagonistic effect of zinc stearate when added to the phenolic antioxidant alone or with the phenol/phosphite blend. These interesting observations led to the investigation of the consumption of both antioxidants, i.e. I1010 and I168, during the multiple extrusion experiment.

Results regarding the consumption of I1010 and I168 during the multiple extrusions showed some very interesting features. The results are presented in Figures 2 and 3. A control formulation containing mLLDPE stabilised with 1000 ppm of I1010 and 1000 ppm of I168 was used as a reference. Two additional control formulations containing respectively mLLDPE stabilised with 1000 ppm of phenolic antioxidant

I1010 only and mLLDPE stabilised with 1000 ppm of phosphite antioxidant I168 only, were also used as references in order to assess the influence of both antioxidants on each other.

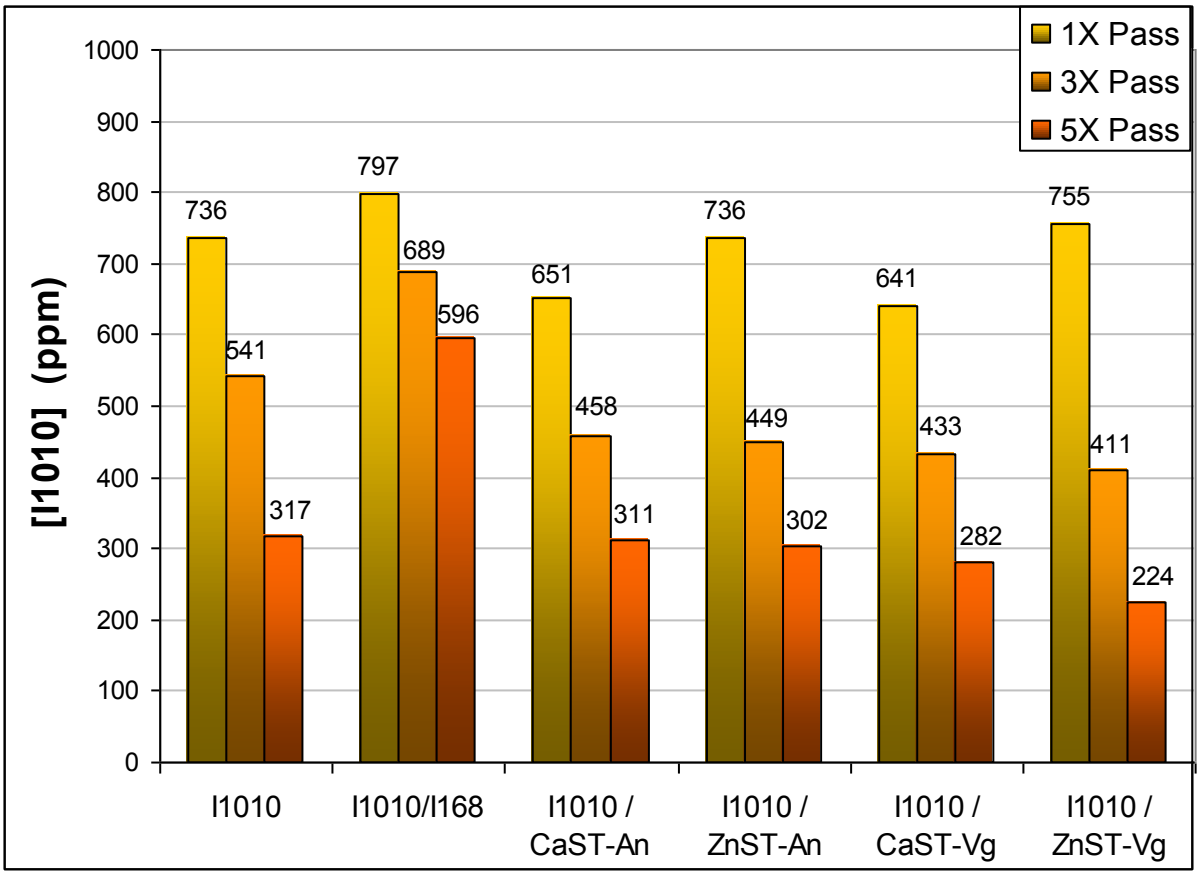

Figure 2. Concentration of I1010 after the first, third and fifth extrusion of mLLDPE stabilised with a phenolic AO I1010 (1000 ppm), a phosphite AO I168 (1000 ppm), and a metal stearate (1000 ppm) at 200°C

First of all, it is noteworthy to underline the sacrificial protection of the phosphite I168 toward the consumption of the phenolic antioxidant I1010 observed in the melt stabilisation of the investigated mLLDPE. Indeed, it is well known that phosphite antioxidants are consumed in a sacrificial way to protect the excessive consumption of phenolic antioxidant during processing. Figure 2 clearly shows that more than 25% of I1010 has been consumed after the first extrusion when mLLDPE was processed with the phenolic antioxidant alone, and that approximately 30% of I1010 only remained after the fifth extrusion. However, when mLLDPE was stabilised with phenol and phosphite antioxidants, 60% of phenolic antioxidant I1010 remains after the fifth extrusion. Figure 3 confirms the sacrificial consumption of phosphite antioxidant I168 toward the protection of the phenolic antioxidant I1010 as 40% of I168 has already been consumed after the first extrusion of mLLDPE stabilised with both antioxidants, and only 20% of I168 remains after the third extrusion. After the fifth extrusion, the phosphite antioxidant I168 was totally consumed.

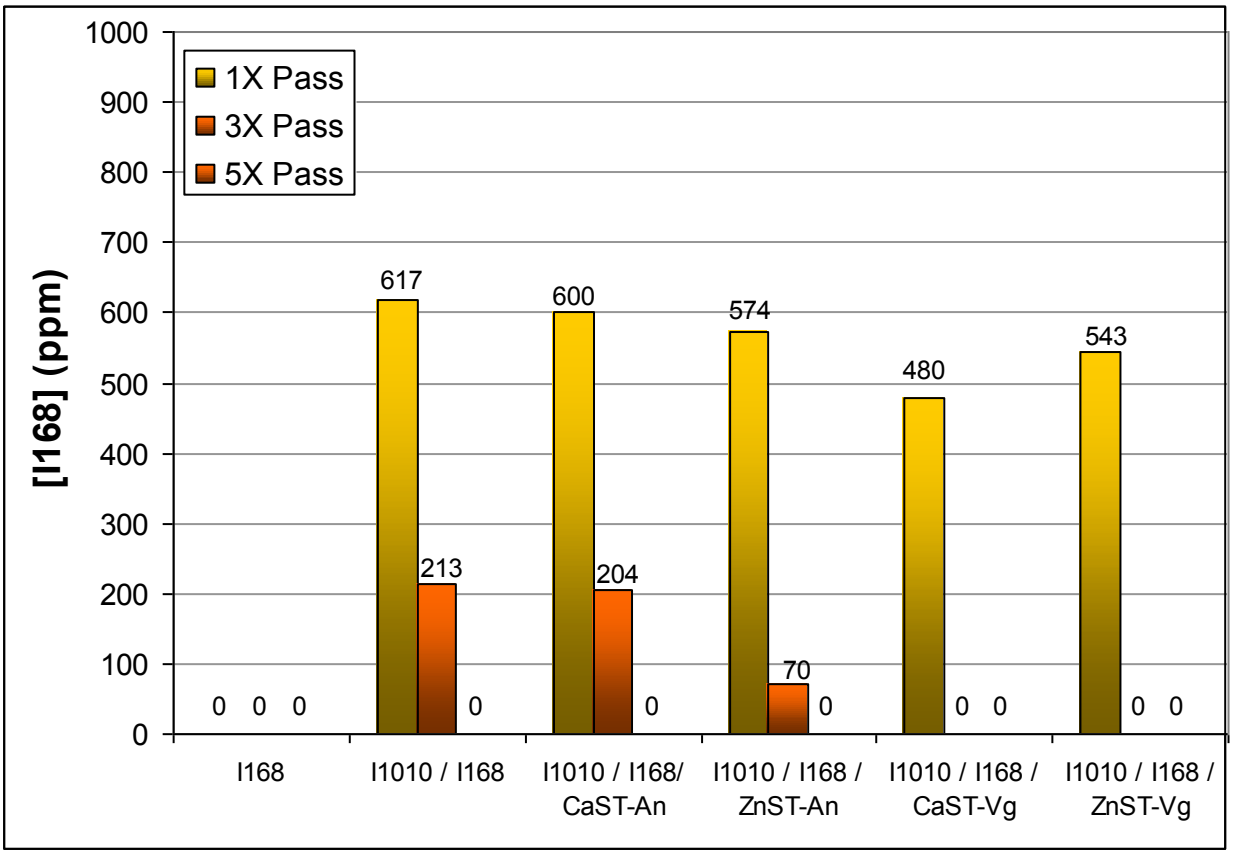

Figure 3. Concentration of I168 after the first, third and fifth extrusion of mLLDPE stabilised with a phenolic AO I1010 (1000 ppm), a phosphite AO I168 (1000 ppm), and a metal stearate (1000 ppm) at 200°C

Figure 4 shows the formation of the oxidative conversion product of the phosphite antioxidant I168, i.e., the corresponding phosphate. It is clear that the absence of phenolic antioxidant does result in a total consumption of the phosphite antioxidant, hence the formation of nearly 85% of the phosphate after the first extrusion.

Regarding the influence of metal stearates on the consumption of the antioxidants, significant features could be observed. A greater consumption of the antioxidants was recorded in the presence of both grades and types of metal stearates. However, a more pronounced detrimental effect was observed for the vegetable-based metal stearates. Indeed, the phosphite antioxidant I168 was totally consumed after the third extrusion of the mLLDPE processed with the vegetable grades of metal stearates (Figure 3). The higher concentration of phosphate conversion product after the third extrusion also supports this excessive consumption of phosphite in the presence of the vegetable grade of metal stearates. Therefore, the presence of metallic salts of fatty acids is accelerating the mechanism of phosphite hydroperoxide decomposition.

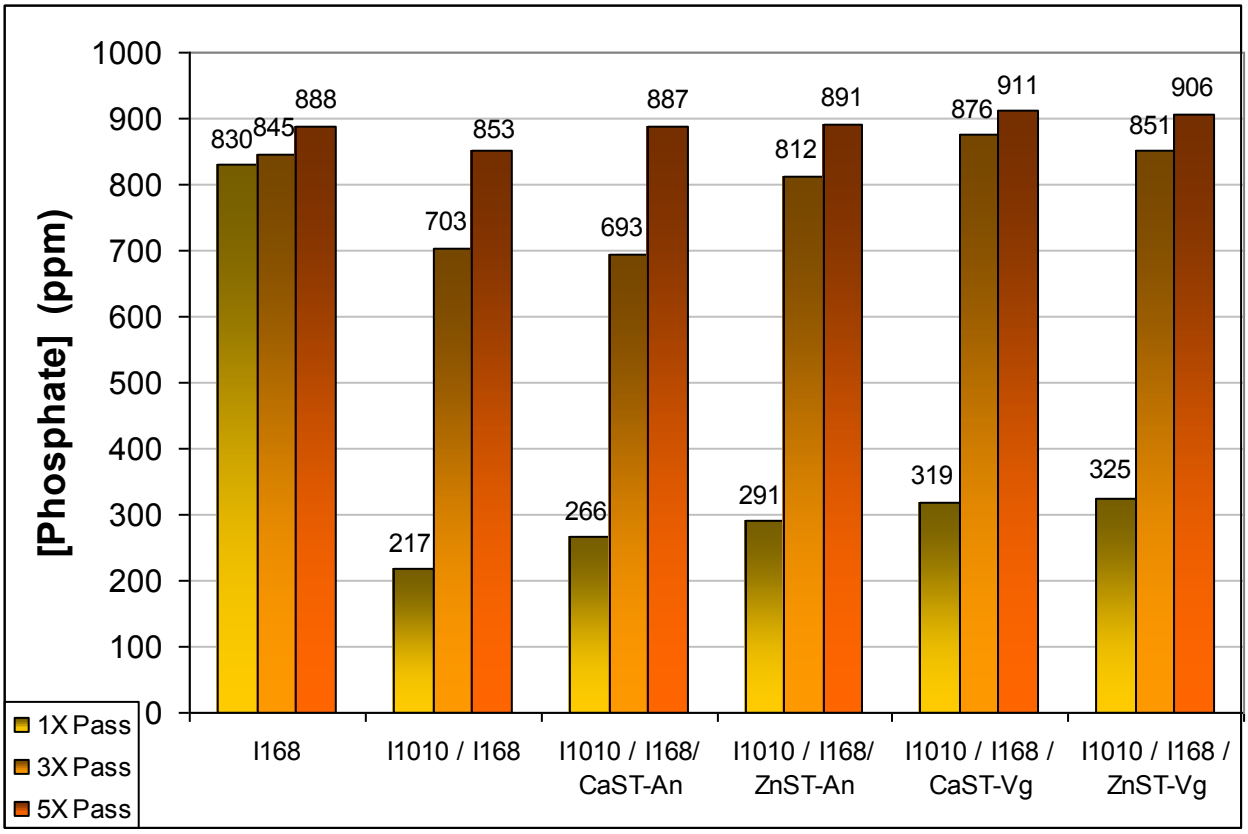

Figure 4. Concentration of Phosphate after the first, third and fifth extrusion of mLLDPE stabilised with a phenolic AO I1010 (1000 ppm), a phosphite AO I168 (1000 ppm), and a metal stearate (1000 ppm) at 200°C

The presence of metal stearates did also have an effect on the higher consumption of the phenolic antioxidant as it can be clearly observed in Figure 2. Although one could argue that the sacrificial protection of the phosphite antioxidant toward the phenolic antioxidant could be sufficient to avoid excessive consumption of the latter, this was not the case in this work. Indeed, after the third extrusion, nearly 70% of the phenolic antioxidant I1010 remained when no metal stearates were added to the bi-blend antioxidant formulation. However, in the presence of metallic stearate, the maximum concentration recovered after the third extrusion was less than 50% of I1010. Here again, vegetable-grades of metal stearates did enhance the consumption of the phenolic antioxidant compared to animal-based metal stearates. This trend was even more pronounced after the fifth extrusion since nearly 60% of the phenolic antioxidant was still present for the formulation containing no acid scavengers, while only approximately 30% of I1010 remained in the presence of the animal-grades of metal stearates, and less than 30% of I1010 was left in the case of the vegetable-based metal stearates.

These interesting results led us to investigate the interactions of both antioxidants individually with the metal stearates. In the case of the phosphite antioxidants, this investigation could not provide any additional information since the phosphite antioxidant was already totally consumed after the first extrusion pass with or without the presence of metal stearates. On the other hand, interesting results were obtained in the case of

the phenolic antioxidant due to its higher performance. Results regarding the consumption of I1010 in the presence of metal stearates are presented in Figure 5.

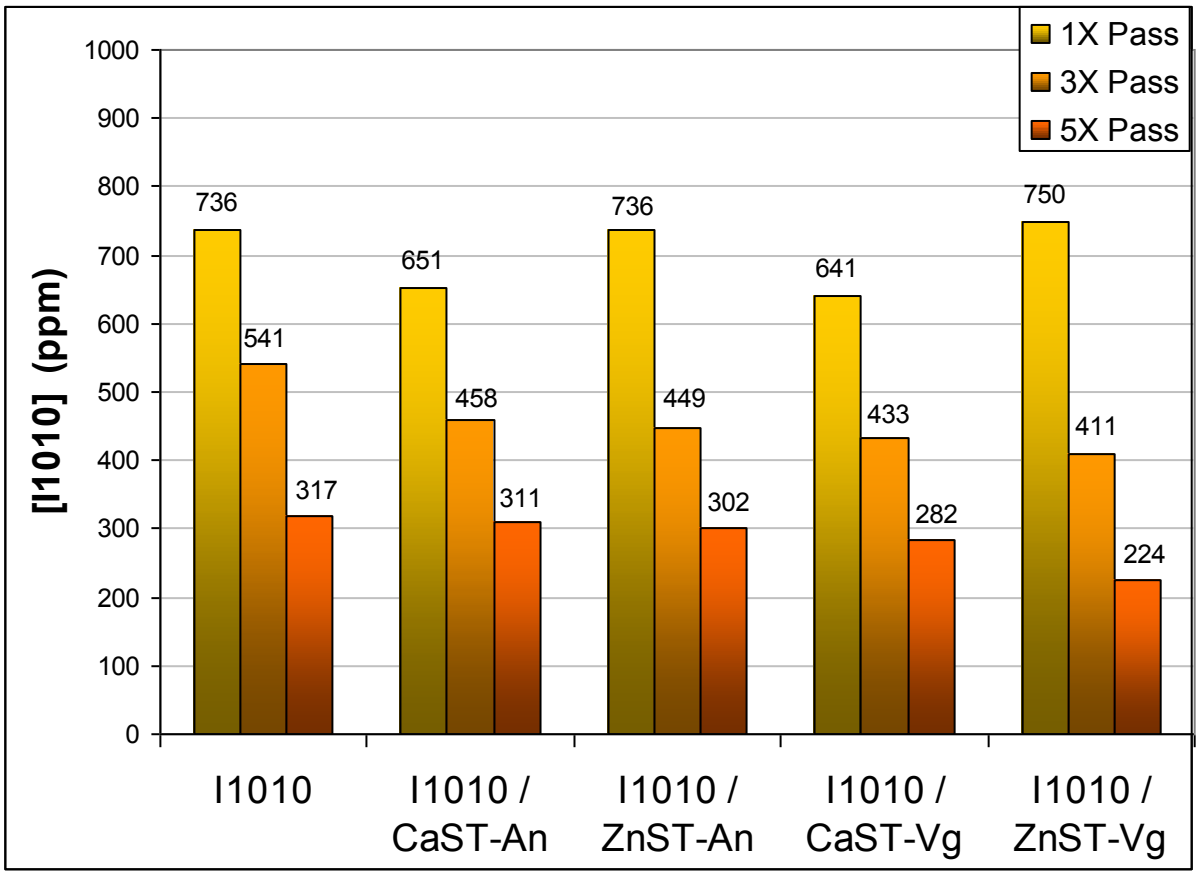

Figure 5. Concentration of I1010 after the first, third and fifth extrusion of mLLDPE stabilised with a phenolic AO I1010 (1000 ppm), and a metal stearate (1000 ppm) at 200°C

A significant consumption of the phenolic antioxidant was observed in the presence of the metal stearates after the third extrusion. Indeed, approximately 55% of I1010 remained after the third extrusion when no metal stearate was present, while not more than around 45% was left when mLLDPE was processed with the metal stearates. After the fifth extrusion, the trend was not as significant as after the third extrusion, but a higher concentration of I1010 was recorded for the formulation containing no metal stearates. Furthermore, a similar trend regarding the effect of the grade of metal stearates was also in accordance with the previous results. A greater consumption after the third and fifth extrusion was observed with the metal stearates produced from the vegetable stearine. Moreover, zinc stearates seemed to provide a greater detrimental effect than calcium stearates, as was also observed previously.

These interesting features regarding the detrimental influence of the presence of metal stearates as well as the more pronounced antagonism exhibited by the vegetable-grades of fatty acid salts motivated an analysis of the stearine sources themselves used for the production of those metal stearates.

Metal stearates are obtained from "commercial" stearic acid or stearine, which is a mixture of palmitic and stearic acid [16]. Table 7 shows the typical composition of the animal-based stearine used in this work. The composition of the animal-based stearine confirms the fact that ratio of C_{18} to C_{16} is either approximately 2:1 in animal-based raw materials.

Table 7: Composition of the animal-based stearine used in this work

Composition	C_{14}	C_{16}	C_{18}	C_{20}
%	3	31	64	1

Stearic acid is a naturally occurring saturated organic acid present in the glycerides of animal fats and most vegetable oils, and is derived from palm, soybean oil or edible tallow. Fats and fatty oils are well known to contain peroxides [16,17]. Therefore, stearine and metal salts of fatty acids may also contain peroxides. Determination of the peroxide value of the stearine sources used for the production of the investigated metal stearates was investigated. Results are presented in Table 8.

Table 8: Peroxide content (meq/kg) of stearine used for the formation of the investigated metal salts of fatty acids

Stearine	Peroxide value (meq/kg)	□	RSD
Animal	1.61 ± 0.04	0.01	0.9
Vegetable	2.04 ± 0.09	0.04	1.77

The results confirmed the presence of peroxides in both stearine blends, and hence in the corresponding metal salts of fatty acid samples. This may therefore account for the greater consumption of the antioxidants in the presence of the metal stearates. Indeed, both investigated antioxidants, i.e., phenol and phosphite, react with peroxide compounds during their mode of action. Sterically hindered phenolic antioxidants act as chain breaking donor by transferring its hydrogen atom to a free peroxy radical $ROO^{\bullet}$ usually produced during the thermal processing operation, while phosphites act as hydroperoxide decomposers and are converted into phosphates. During processing the stearates may also oxidise in the melt extrusion process.

Therefore, the level of metal stearate must be optimised with care, especially with certain grades of polyethylene wil levels of various catalyst residues, in order to avoid excessive antagonistic interactions with the phenolic and phosphite antioxidants that may impare the stabilisation performance of the overall stabiliser formulation.

4.2 Optimisation of Phenol/Phosphite Combinations

The optimisation of the stabilisation of metallocene polyethylene has been investigated in this study. Several conditions of stability were required for the determination of the optimal antioxidant (phenol:phosphite) package. The main parameter was high melt stability for a maximum processing stability of the final package (OIT). Long-term stability against thermo-oxidation was obviously required. Hydrolytic stability was also an important factor. It has been decided that phosphites exhibiting high hydrolytic stability was important and discoloration had to be avoided.

This work optimised the (phenol/phosphite) antioxidant package with two different phenolic antioxidants (Irganox 1010, Irganox 1076) and six different phosphite antioxidants (Irgafos 168, Irgafos P-EPQ, Adekastab PEP-8, Adekastab PEP-36, Adekastab PEP-24G, Adekastab HP-10). Different levels were set for determining the best synergistic (phenol/phosphite) package:

-0.1% w/w phenolic controls

-0.1% w/w phosphite controls

-0.1% w/w (phenolic/phosphite) package at different ratios (4:1, 3:2, 2:3, 1:4)

Oven ageing at 110C was followed. Spectroscopic measurements for the determination of carbonyl growth was then assessed on films pressed after solvent blending. Colour development was also determined according to ASTM 1925. Thermal stability was also assessed by Differential scanning calorimetry (DSC) via the determination of an oxygen induction time (OIT).

In the data analysis only the best performing formulations are summarized and shown for clarity and comparison here.

Hydrolytic stability

In the first instance the hydrolytic stability of the phosphites studied here were determined and shown in Table 9. It is clear that Alkanox 28 exhibits outstanding hydrolytic stability compared to the other phosphites. Adekastab HP-10 displays higher hydrolytically stability than Irgafos 168. Adekastab PEP-36 is twice more hydrotically stable than Irgafos P-EPQ, which is considered as hydrotically unstable. Adekastab PEP-24G as well as Adekastab PEP-8 are worse than Irgafos P-EPQ in term of hydrolytic stability. Although it is possible to reduce this problem through admixture with for example hydrotalcite this can have implications in some formulations.

Table 9

Phosphites	**Induction time (hours) for the complete hydrolysis of th phosphites under water vapor at 80C**
Alkanox 28	335
HP-10	23
Irgafos 168	15.5
Adekastab PEP-36	9
Irgafos P-EPQ	5
Adekastab PEP-24G	4.5
Adekastab PEP-8	Very low

OIT data

From the OIT analysis many of the formulations gave values of less than 20 minutes at the 200 ^{o}C test. Those which outperformed in terms of the best ten are illustrated in Table 10. The Irganox 1010: Adekastab PEP-24G at a ratio of 3:2 gave the best performance. Alkanox 28 and the Irgafos P-EPQ exhibited very low performance in comparison. In general Irganox 1076 unlike that of Irganox 1010 required higher ratios of phosphite.

Table 10

Best Performing Phenol:Phosphite formulations using OIT

Ranking Order	(phenol:phosphite) package	OIT (minutes)
1	3:2 Irganox 1010:Adekastab PEP-24G	140
2	3:2 Irganox 1076:Adekastab HP-10	107
3	4:1 Irganox 1010:Adekastab PEP-8	95
4	4:1 Irganox 1010:Adekastab PEP-36	70
5	1:4 Irganox 1076:Adekastab HP-10	69
6	4:1 Irganox 1010:Irgafos 168	66
7	2:3 Irganox 1010:Adekastab PEP-24G	59
8	2:3 Irganox 1076:Adekastab HP-10	57
9	4:1 Irganox 1010:Adekastab HP-10	52
10	3:2 Irganox 1010:Adekastab HP-10	50

After considering the hydrolytic stability of the phosphites, only seven formulations remain, that are shown in Table 11.

Table 11

Best Performing Phenol: Phosphite Forulations for OIT taking into Account Hydrolysis

Ranking Order	(phenol:phosphite) package	OIT (minutes)
1	3:2 Irganox 1076:Adekastab HP-10	107
2	4:1 Irganox 1010:Adekastab PEP-36	70
3	1:4 Irganox 1076:Adekastab HP-10	69
4	4:1 Irganox 1010:Irgafos 168	66
5	2:3 Irganox 1076:Adekastab HP-10	57
6	4:1 Irganox 1010:Adekastab HP-10	52
7	3:2 Irganox 1010:Adekastab HP-10	50

Oven ageing data

The following table is showing the ten best packages that exhibit high long-term stability against thermo-oxidation. Unlike the OIT data oven ageing was poor for Irgamox 1076 leaving only the Iragnox 1010 formulations of any interest. The 4:1 Irganox 1010: Irgafos P-EPQ exhibiting the greatest performance.

Table 12

Best Performing Phenol:Phosphite formulations using Oven Ageing

Ranking Order	(phenol:phosphite) package	Embrittlement time (hours)
1	4:1 Irganox 1010:Irgafos P-EPQ	2772
2	3:2 Irganox 1010:Adekastab PEP-36	2628
3	4:1 Irganox 1010:Adekastab HP-10	2534
4	4:1 Irganox 1010:Adekastab PEP-24G	2528
5	4:1 Irganox 1010:Adekastab PEP-36	2525
6	3:2 Irganox 1010:Adekastab PEP-8	2523
7	2:3 Irganox 1010:Irgafos 168	2490
8	3:2 Irganox 1010:Irgafos P-EPQ	2437
9	4:1 Irganox 1010:Irgafos 168	2431
10	4:1 Irganox 1010:Adekastab PEP-8	2252

After considering the hydrolytic stability of the phosphites, only five formulations remain, as is shown in table 10.

Table 10

Best Performing Phenol:Phosphite formulations using Oven Ageing taking Hydrolysis into Account

Ranking Order	(phenol:phosphite) package	Embrittlement time (hours)
1	3:2 Irganox 1010:Adekastab PEP-36	2628
2	4:1 Irganox 1010:Adekastab HP-10	2534
3	4:1 Irganox 1010:Adekastab PEP-36	2525
4	2:3 Irganox 1010:Irgafos 168	2490
5	4:1 Irganox 1010:Irgafos 168	2252

Yellowness Index data

The following table is showing the ten best packages that exhibit lowest discoloration against thermo-oxidation. This test is a crucial factor in polyolefin technology especially clear films and sheets. Many of the 4:1 formulations rated well all being Irganox 1010 with the Irganox 1076 formulations exhibiting extreme colour in our tests.

Table 11

Best Performing Phenol:Phosphite formulations using Yellowness Index

Ranking order	(phenol:phosphite) package	Yellowness Index at 2736 hours of oven ageing
1	3:2 Irganox 1010:Adekastab PEP-8	1.71
2	4:1 Irganox 1010:Irgafos P-EPQ	4.71
3	4:1 Irganox 1010:Adekastab HP-10	7.6
4	3:2 Irganox 1010:Adekastab PEP-36	9.72
5	3:2 Irganox 1010:Irgafos P-EPQ	12.07
6	4:1 Irganox 1010:Adekastab PEP-36	14.36

7	4:1 Irganox 1010:Adekastab PEP-24G	19.91
8	4:1 Irganox 1010:Irgafos 168	20.53
9	2:3 Irganox 1010:Irgafos 168	25.08
10	4:1 Irganox 1010:Adekastab PEP-8	26.76

After considering the hydrolytic stability of the phosphites, only five formulations remain, as is shown in table 12 with the 4:1 Irganox 1010: Adekastab HP-10 exhibiting the best criteria on this factor.

Table 12

Best Performing Phenol:Phosphite formulations using Yellowness Index taking Hydrolysis into Account

Ranking Order	(phenol:phosphite) package	Yellowness Index at 2736 hours of oven ageing
1	4:1 Irganox 1010:Adekastab HP-10	7.6
2	3:2 Irganox 1010:Adekastab PEP-36	9.72
3	4:1 Irganox 1010:Adekastab PEP-36	14.36
4	4:1 Irganox 1010:Irgafos 168	20.53
5	2:3 Irganox 1010:Irgafos 168	25.08

Final synergistic (phenol/phosphite) Formulation

The following tables summarize the best ratios in terms of melt stability, long-term stability and discoloration.

Table 13

Best Formulations of melt stability, long-term stability and discoloration

Ranking Order	(phenol:phosphite) package	OIT (minutes)
1	3:2 Irganox 1076:Adekastab HP-10	107
2	4:1 Irganox 1010:Adekastab PEP-36	70
3	1:4 Irganox 1076:Adekastab HP-10	69
4	4:1 Irganox 1010:Irgafos 168	66
5	2:3 Irganox 1076:Adekastab HP-10	57
6	4:1 Irganox 1010:Adekastab HP-10	52
7	3:2 Irganox 1010:Adekastab HP-10	50

Ranking Order	(phenol:phosphite) package	Embrittlement time (hours)
1	3:2 Irganox 1010:Adekastab PEP-36	2628
2	4:1 Irganox 1010:Adekastab HP-10	2534
3	4:1 Irganox 1010:Adekastab PEP-36	2525
4	2:3 Irganox 1010:Irgafos 168	2490
5	4:1 Irganox 1010:Irgafos 168	2252

Ranking Order	(phenol:phosphite) package	Time at which YI=1 (hours)
1	4:1 Irganox 1010:Adekastab HP-10	2440
2	4:1 Irganox 1010:Adekastab PEP-36	2395
3	4:1 Irganox 1010:Irgafos 168	2370
4	3:2 Irganox 1010:Adekastab PEP-36	2310
5	2:3 Irganox 1010:Irgafos 168	2270

Finally, only three packages satisfy all the required conditions of stability with Yellowness playing an important role as well as hydrolysis:

- 4:1 Irganox 1010:Adekastab PEP-36
- 4:1 Irganox 1010:Irgafos 168
- 4:1 Irganox 1010:Adekastab HP-10

The following table is summarising the ranking order (1,2,3,4) of the selected packages that satisfy all the required conditions of stability.

Table 14

Final 3 Formulations and Performance Rating

(phenol:phosphite) package	Hydrolytic stability	Melt stability	Long-term stability	Discoloration
4:1 Irganox 1010:Adekastab PEP-36	3	**1**	2	2
4:1 Irganox 1010:Adekastab HP-10	**1**	3	**1**	**1**
4:1 Irganox 1010:Irgafos 168	2	2	3	3

From the data the embrittlement time of the formulation containing PEP-36 is very close from the value of the package containing HP-10 (a difference of 9 hours only). Then both packages exhibit about the same long-term performance. Even if the formulation containing HP-10 is slightly less discolored than the package containing PEP-36 no outstanding differences in terms of discoloration were noticed between them. The main relevant parameter that can then differentiate the two formulations is their OIT melt stability. Indeed, the formulation containing PEP-36 displays significantly higher melt stability than that containing HP-10 as is shown in Table 14.

5. CONCLUSIONS

This study follows on from much of our extensive earlier studies [4-8] in examining the performance characteristics of a phenol/phosphite combination at 1000ppm each through multiple extrusion processes in a metallocene LLDPE (mLLDPE) while investigating for the first time the role of a broad range of calcium and zinc stearates based on both animal vs vegetable origins of the stearine function. Both stearates influenced the thermal activity of the antioxidants in particular their consumption during processing. A greater consumption after the third and fifth extrusion was observed with metal stearates produced from the vegetable stearine. Moreover, zinc stearates seemed to provide a greater detrimental effect than calcium stearates. Hydroperoxide analysis on the stearates confirmed the animal stearine to contain higher levels of peroxides which may contribute toward their higher activity. The optimisation of the thermal stabilisation of the metallocene polyethylene (mLLDPE) has also been investigated in this study for a widely used phenolic/phosphite combination. Long-term stability against thermo-oxidation coupled with a consideration of their hydrolytic stability as a complicating factor were considered in the outcome. In this work the (phenol/phosphite)

antioxidant formulations with two different phenolic antioxidants (Irganox 1010, Irganox 1076) and six different phosphite antioxidants (Irgafos 168, Irgafos P-EPQ, Adekastab PEP-8, Adekastab PEP-36, Adekastab PEP-24G, Adekastab HP-10) were assessed at different levels taking into account the various criteria for optimal performance providing hitherto useful information than many prior studies. A question often posed in the world of polymer technology with the results here conclude some interesting data. However, the field of polyolefin stabilization is very wised and encompassing involving multiple formulations in many applications for specific purposes each one having its own complications. The data outcomes here like many academic/laboratory probes should serve to provide atleast some insights into possible parameters that may have to be considered when formulating in the real world.

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